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(71) Applicant: 000005083
Hitachi Metals KK
1-2-1 Shibaura, Minato-ku, Tokyo-to
(71) Applicant: 000109543
Terumo KK
2-44-1 Hatagaya, Shibuya-ku, Tokyo-to
(72) Inventor: Motoi YAMAGUCHI
Hitachi Research Laboratory, Hitachi Metals KK
2107-2 Yasugi-cho, Yasugi-shi, Shimane-ken
(74) Agent: 100074848
Hiroshi MORITA, Patent Attorney

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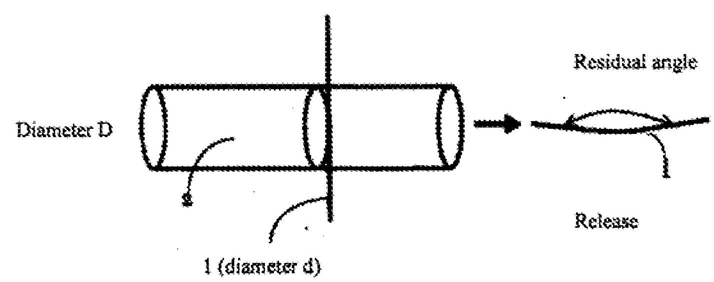
(54) Title of the Invention: A material for a guide wire and the method for producing the same

(57) Abstract:
[Problem to be Solved] To provide a material for a guide wire whereby the problems of harmfulness, embrittlement and hot working properties in the process of production of the material for a guide wire are solved, and that is provided with strength, hardness, kink resistance and torque transferability as well, and to provide a method for producing the same.
[Solution] The material for a guide wire has a composition containing by mass ≤ 0.2% C, 0.1 to 2.0% Si, 0.1 to 3.0% Mn, 30 to 76% Co, 10 to 40% Ni, 10 to 30% Cr and 3 to 20% Mo, and further containing as impurities ≤ 0.01% O, ≤ 0.02% S and < 0.03% (inclusive of 0%) Be, with the remnant being substantially Fe.



[Scope of Claims]

[Claim 1] A material for a guide wire, characterized in that it has a composition containing by mass ≤ 0.2% C, 0.1 to 2.0% Si, 0.1 to 3.0% Mn, 30 to 76% Co, 10 to 40% Ni, 10 to 30% Cr and 3 to 20% Mo, and further containing as impurities ≤ 0.01% O, ≤ 0.02% S and < 0.03% (inclusive of 0%) Be, with the remnant being substantially Fe.

[Claim 2] The material for a guide wire described in Claim 1, wherein it further contains by mass less than 5% total of one or two or more among Ti, Al and Nb.

[Claim 3] The material for a guide wire described in Claim 1 or 2, wherein when the guide wire is wound once and released along the outer periphery of a round bar where the ratio D: d of the diameter (D) [of the round bar] to the diameter (d) of the material used for the guide wire equals 25-80: 1, the angle created by the lines of both sides of the winding site is 150° or more.

[Claim 4] The material for a guide wire described in any one of the claims from Claim 1 to 3, wherein when one end of the material for a guide wire with a length of 1 m is rotated in the area around the central axis, the other end, which is loaded with a torque of 11.3 mN•m per unit sectional area (1 mm^2) of said material, responds with a lag of 25 seconds or less and rotates, and moreover the above-mentioned rotation that occurs in response does not oscillate periodically or its period is 20 seconds or less.

[Claim 5] A method for producing a material for a guide wire, being the method for producing the guide wire described in any one of the claims from Claim 1 to 4, wherein aging at 300-700 °C is carried out after cold working at a surface reduction rate of 20% or more.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains] The present invention relates to a method for producing a material for a guide wire for introducing a catheter, which is a medical device, to the prescribed locus such as a blood vessel, the heart, digestive tract, trachea or some other body cavity.

[0002]

[Prior Art] When a catheter is introduced to the prescribed locus such as a blood vessel, a guide wire for the purpose of guiding the former is introduced to the target part. In order to be able to handle blood vessels, etc., which branch and wind in complicated ways, the tip part of the guide wire must possess adequate flexibility. This flexibility is ensured by making the tip of the guide wire thin or by connecting a different kind of material to only the end part. In addition, sufficient strength and hardness are required in order that the rotation operated by the surgeon at the manual operation part in order to control the guide wire is all substantially transmitted to the tip part (torque transferability), and it is moreover possible to extrude [the catheter] without its buckling inside the blood vessel, etc.

[0003] Strength and hardness are particularly needed in the hands of the physician operating the guide wire, and it is also necessary that no kinking (permanent deformation) occur even when the guide is passed through winding blood vessel, etc. When such kinking occurs, the rotation is not transferred in the desired state, and manually operated rotation ends up being a whipping motion. As indicated above, strength, hardness, torque transferability, kink resistance and as need requires flexibility are sought as the characteristics required for a material for a guide wire, and in particular strength, hardness, torque transferability and kink resistance are the characteristics sought as necessary for the materials.

[0004] Conventionally, SUS304 or SUS302 type (JIS G4309) stainless steel, which is subjected to cold plastic working in order to raise its strength greatly (see for example Unexamined Japanese Patent Application Bulletin No. H11[1999]-299899, Unexamined Japanese Patent Application Bulletin No. H06[1994]-063150, etc.), or Ni-Ti alloy, which is an ultra-elastic alloy (see for example Unexamined Japanese Patent Application Bulletin No. 2001-009041, Unexamined Japanese Patent Application Bulletin No. H11[1999]-128363, etc.), are commonly employed as the material for a guide wire for which such characteristics are sought. However, when it comes to stainless steel, there is room for improvement of strength, hardness and torque transferability of the advantageous kinds of conventional materials, and the kink resistance of these materials is inadequate. Although the Ni-Ti alloy is superior in kink resistance, it is conspicuously inferior when it comes to strength, hardness and torque transferability.

[0005]

[Problems That the Invention Attempts to Solve] In order to address the above-described problems, it has been proposed that a Co-Ni-Cr-Fe-based alloy and Elgiloy (trademark of the Elgiloy company; hereinafter abbreviated simply as "Elgiloy"), which improves the kink resistance, strength and hardness while possessing superior torque transferability, be employed for the guide wire. Specifically, there is a proposal in Japanese Patent Document No. H11[1999]-502434 that Elgiloy alloy be employed as the shaft material of the guide wire as an example in which the kink resistance is improved, and there is a disclosure in Unexamined Japanese Patent Application Bulletin No. H06[1994]-63151 of the employment of a Co-Ni-Cr-Fe-based alloy with the same composition as Elgiloy alloy as the material of a guide wire as an example in which the strength and hardness are improved.

[0006] Although the above-described Co-Ni-Cr-Fe-based alloy and Elgiloy alloy disclosed in Japanese Patent Document No. H11[1999]-502434 and Unexamined Japanese Patent Application Bulletin No. H06[1994]-63151 are advantageous in terms of their strength, hardness, torque transferability and kink resistance, this Elgiloy alloy and Co-Ni-Cr-Fe-based alloy contain a small amount of Be, which is a harmful element, so there are concerns about the potential for an adverse effect on the human body during production of the material for a guide wire. There is a potential for the problem of Be to become a problem in terms of practical application of a guide wire composed of the Elgiloy alloy or a Co-Ni-Cr-Fe-based alloy that is similar to it.

[0007] In addition, since no Si has been added to these alloys, the deoxidation is inadequate, and a large amount of O remains and the material for a guide wire becomes brittle, and there are concerns that it will break during cold working or during use. Moreover, in the case of the Elgiloy alloy and Co-Ni-Cr-Fe-based alloy disclosed in Japanese Patent Document No. H11[1999]-502434 and Unexamined Japanese Patent Application Bulletin No. H06[1994]-63151, the amount of S, which is an impurity element, has not been taken into account, and there are the problems that the cold working properties are poor due to the S content, and cracking is caused during hot working, which is a necessary process during production. The purpose of the present invention is to provide a material for a guide wire whereby the problems of harmfulness, embrittlement and hot working properties in the process of production of the material for a guide wire are solved, while it maintains the superior strength, hardness, torque transferability and kink resistance possessed by the Elgiloy alloy and Co-Ni-Cr-Fe-based alloy that have been employed to date, and to provide a method for producing the same.

[0008]
[Means for Solving the Problems] The present inventors, et al examined the problems of the harmfulness, embrittlement and hot working properties in the process of production of the material for a guide wire, and the result was that they discovered that it is possible to improve the harmfulness, embrittlement and hot working properties during the production thereof by adding the absolute minimum amount of Si, and restricting the amount of O and S, which are impurities, to a minimum, and moreover not adding (0%) Be and controlling it to the impurity level, and thereby arrived at the present invention.

[0009] In other words, the present invention is a material for a guide wire, characterized in that it has a composition containing by mass ≤ 0.2% C, 0.1 to 2.0% Si, 0.1 to 3.0% Mn, 30 to 76% Co, 10 to 40% Ni, 10 to 30% Cr and 3 to 20% Mo, and further containing as impurities ≤ 0.01% O, ≤ 0.02% S and < 0.03% (inclusive of 0%) Be, with the remnant being substantially Fe. Preferably, it is a material for a guide wire that further contains by mass less than 5% total of one or two or more among Ti, Al and Nb.

[0010] In addition, the present invention is a material for a guide wire wherein when the guide wire is wound once and released along the outer periphery of a round bar where the ratio D: d of the diameter (D) [of the round bar] to the diameter (d) of the material used for the guide wire equals 25-80: 1, the angle created by the lines of both sides of the winding site is 150° or more, and is a material for a guide wire wherein when one end of the material for a guide wire with a length of 1 m is rotated in the area around the central axis, the other end, which is loaded with a torque of 11.3 mN•m per unit sectional area (1 mm^2) of said material, responds with a lag of 25 seconds or less and rotates, and moreover the above-mentioned rotation that occurs in response does not oscillate periodically or its period is 20 seconds or less.

[0011] In addition, the present invention is a method for producing a material for a guide wire, being the method for producing the guide wire wherein aging at 300-700 °C is carried out after cold working at a surface reduction rate of 20% or more.

[0012]
[Mode of Embodiment of the Invention] As described above, the important characteristic of the present invention is that the harmfulness, embrittlement and hot working properties are improved during the production of the material for a guide wire by adding the absolute minimum amount of Si, and restricting the amount of O and S, which are impurities, to a minimum, and moreover not adding (0%) Be and controlling it to the impurity level, while the superior strength, hardness, torque transferability and kink resistance possessed by the Elgiloy alloy and Co-Ni-Cr-Fe-based alloy that have been employed to date are maintained. A description is provided below about the action of each element.

[0013] C not only forms a solid solution in the base and carries out solid solute strengthening of the base, but also bonds with Cr, etc. to form a carbonate, and this has the effects of raising the elastic limit and preventing grain coarsening. However, when it is added to excess, this increases the work hardening of the base, and moreover causes a decline in the cold working properties due to formation of a large amount of carbonate, and in addition results in a lack of Cr in the base and thereby lowers the corrosion resistance. Therefore, C is limited to 0.2% or less. Preferably it is 0.15% or less. In addition to the fact that Si exhibits powerful deoxidizing action towards molten metal, it has the action of improving the casting properties, so the addition of Si is required in the present invention. However, when the amount of Si is less than 0.1%, the O content increases, and a large amount of O remains and this causes the material for guide wire to become brittle. On the other hand, when in excess of 2.0% is added, the cold working properties decline, so the amount of Si is set at 0.1 to 2.0%, and preferably the content of Si is in a range of 0.1 to 1.0%.

[0014] In addition to the fact that Mn exhibits the same deoxidation action as Si, it has the action of improving casting properties, but when an excess amount is added this blocks the precipitation of the εCo phase, and thus it is stipulated that Mn is set at 0.1 to 3.0% in order to bring about a decline in the strength and hardness. Preferably it is in a range of 1.0 to 2.5%. Co is the element that serves as the base of the present alloy, and it is transformed from the αCo phase to the εCo phase by cold working and aging, and moreover it moreover precipitates an intermetallic compound and improves the strength, hardness and torque transferability by aging. When the amount of Co is less than 30%, there are no effects, whereas there is no effect of further improvement in the strength even if it is added in excess of 76%, so it is stipulated that Co is set at 30 to 76%. Preferably it is in a range of 35 to 45%.

[0015] Ni is an element that causes softening to a hardness at which cold working can be done by solution treatment, and that bonds with Ti and/or Al in aging to precipitate a γ' phase, and thereby contributes to the hardness. When the amount of Ni is less than 10%, there are few effects, whereas when it is added in excess of 40% it blocks the transformation to the εCo phase required for improving the strength, hardness and torque transferability, so it is stipulated that the amount of Ni added is 10 to 40%. Preferably it is in a range of 10 to 20%. Cr is an element that forms carbonates and raises the elastic limit, and in addition precipitates in the base, and maintains corrosion resistance that is required when it is inserted in vivo, and owing to this addition of 10% or more thereof is required. However, when it is added in excess of 30%, the cold working properties decline, so the amount of Cr is set at 10 to 30%. Preferably it is in a range of 15 to 25%.

[0016] Mo is an element that not only forms a solid solution in the base, and improves the strength and corrosion resistance, but also partially precipitates an intermetallic compound by aging and thereby improves the strength, hardness and torque transferability. When the amount of Mo added is less than 3%, adequate effects are not obtain whereas when it is added in excess of 20% this causes a decline in the working properties, so the amount of Mo added is set at 3 to 20%. Preferably it is in a range of 5 to 15%. Fe is an element that causes a decline in cold working properties like Ni, and it becomes the remnant of each element stipulated by the present invention. However, when it contains an excess of Fe, it causes a decline in the strength, hardness and torque transferability, such as blocking the transformation to the εCo phase, so the preferred upper limit of Fe is 46%, and still more preferably it is 20% or less.

[0017] A description is provided next of the impurity elements that should be limited in the present invention. First of all, O is an impurity element that is unavoidably mixed into the materials during casting. Owing to this, it is necessary to reduce the amount thereof as much as possible by compound addition of Si and Mn, which have a deoxidation effect. When the amount of O is greater than 0.01%, a large amount of inclusion of a oxide system is formed, and there is a possibility that it will break during cold work or during use, so it is set at 0.01% or less.

Preferably it is in a range of 0.005% or less. S is an impurity element that unavoidably mixes into the material during casting, and is an element that causes a decline in the hot working properties, so it is necessary to reduced as much as possible the amount of S by selection of a raw material with a low S content, vacuum decomposition, slag desulphurization, etc. When the amount of S is greater than 0.02%, the hot working properties decline greatly, so the amount of S is set at 0.02% or less. Preferably it is 0.01% or less.

[0018] Be is an element that increases the toughness by aging and precipitation, and since there is the possibility that it will become harmful during the production of the material for a guide wire it is necessary to control it to the unadded level (0%). Assuming that the amount of Be is set at the unadded level (0%), there are no adverse effects on the hardness, strength, kink resistance, torque transferability or other characteristics required for the material for a guide wire in the case of the inventive alloy. In order to eliminate the harmfulness of Be during production, it is necessary to restrict the amount contained to an absolute maximum of less than 0.03%. More preferable is a level of 0.01% or less.

[0019] A description is provided next about the selection elements stipulated in the present invention. Since Ti, Al and Nb are elements that bond with Ni during aging and cause the precipitation of the γ' or γ'' phase of $Ni_3(Ti, Al, Nb)$, and thereby improve the strength, hardness and torque transferability, these are added as need requires. However, when they are added to excess, this causes a decline in the working properties, so the amount of Ti, Al and Nb added is less than 5% total for one kind or two or more kinds thereof. In the present invention, there are no particular stipulations as concerns the impurity elements that are unavoidably contained other than the elements that have been described, but the following elements may be contained in the inventive material within the following range by mass %. $P \leq 0.04\%$, $Cu \leq 0.30\%$, $V \leq 0.5\%$, $Ta \leq 0.5\%$, $Ca \leq 0.02\%$, $Mg \leq 0.1\%$, $N \leq 0.1\%$, $B \leq 0.01\%$.

[0020] Next, it is possible to satisfy the following properties for the above-described inventive material for a guide wire by combining it with an optimal production method. In order to prevent the occurrence of kinking when it passes through the inside of a winding blood vessel, as shown in Figure 1, a round bar (2) with diameter (D) and a material for a guide wire (1) with diameter (d) are prepared so that the ratio of D: d equals 25-80: 1, and it is important when the material for a guide wire (1) is wound once around the round bar (2) at 37 °C and released, the angle created by the lines on both sides of the winding site is 150° or more, and this serves as a key index for knowing whether or not superior kink resistance has been obtained. Here, the reason why the ratio of the round bar diameter (D) and the diameter (d) of the material for the guide wire is set at 25-80: 1 is that a blood vessel that winds inside the human body is envisaged, and the most stringent conditions have been set. Then, assuming that the angle created by the lines on both sides of the winding site is 150° or more when material for a guide wire (1) is wound once and released, it can be judged to be an item whose kink resistance is superior.

[0021] In addition, next, when the inventive material for a guide wire is employed as a guide wire, it enters a state where torque is loaded due to the resistance of the blood. In reality, while there is resistance by the blood (blood flow), [if] the time until the tip part, for which the rotations imparted with the handheld part of the guide wire by the physician are several tens of cm to approximately 1 m, rotates is short, and moreover either the guide wire itself does not oscillate periodically due to the rotation, or if the period is 20 seconds or less even when it does, the ease of operation of the guide wire itself will decline markedly. Owing to this, resistance of blood (blood flow) is envisaged, and in a state in which torque of 11.3 mN•m per unit section area (1 mm^2) of the material for a guide wire is loaded on the other end at 37 °C, the transfer of the rotation in the area around the central axis at the first end, which serves as the handheld part in the material for a guide wire with a length of 1 m, to the other end with a lag of a response time of 25 seconds or less, is sought for the material for a guide wire. If the conditions are met that when the one end of the material for a guide wire whose length is here stipulated at 1 m is rotated in the area around the central axis, the other end, which is loaded with a torque of 11.3 mN•m per unit section area (1 mm^2) of the material for a guide wire, responds and rotates with a lag of within 25 seconds, and moreover the rotation that occurs due to the above-mentioned response either does not oscillate periodically or the period thereof is 20 seconds or less, then it can be judged that good torque transferability has been obtained.

[0022] The response time as used here means the time after the time to the extent that the rotation has started has elapsed as shown in the left figure in Figure 2, until the rotation of the handheld part is transmitted to the tip part (other end), and particularly in the event that there are oscillations in the rotation of the tip part, it is preferable to search for the response time at the inflection point of the curve showing the rotation of the tip part. In the event that there are oscillations in the rotation of the tip part, the time from the same phase until the same phase may basically be sought by for example a method like searching for the time of the inflection point 3 point part, as shown in the right figure in Figure 2.

[0023] A description is next provided of the method of production in the present invention. Cold working and aging are processes required in order to employ the inventive material for a guide wire as a guide wire, and after the chemical composition stipulated by the present invention is satisfied, it is not possible to satisfy simultaneously the strength, hardness, torque transferability and kink resistance unless cold working and aging are applied. By applying cold working and aging, a portion of the αCo phase is transformed into the εCo phase, and moreover an intermetallic compound and carbonates are precipitated during the aging, and owing to this strength, hardness and torque transferability are markedly improved. In the event that the surface reduction rate during cold working is less than 20% and in the event that the aging temperature is less than 300 °C or exceeds 700 °C, the transformation into the εCo phase is inadequate, and in addition it is not possible to obtain adequately an improvement in the strength, hardness and torque transferability by precipitation at this aging temperature. The εCo phase ends up decomposing particularly at temperatures exceeding 700 °C. Therefore, the surface reduction rate in cold working is set at 20% or higher, and the aging temperature following on that is set at 300 to 700 °C. The preferred surface reduction rate for cold working is 40% and higher, and the preferred aging temperature is 450 to 600 °C.

[0024] In addition, the kink resistance is improved by applying aging within the temperature range in the present invention. The strain imparted in cold working by aging recovers, and is reduced. For example, strain in the tensile direction is imparted in cold working such as drawing, and that strain is reduced by the subsequent aging. When the strain in the tensile direction lingers, compressive stress is applied to the inside of the material when the material for a guide wire is bent, ...

... so the phenomenon that it yields at a low strain amount due to the Bauschinger effect occurs. Owing to this, even if it is bent with a large curvature, it deforms plastically with ease, and the kink resistance declines. Therefore, aging is a necessary process for improving the kink resistance, and moreover it does not recover even if the aging temperature is too low and tensile strain lingers, so in this sense as well it is necessary for the aging temperature to be 300 °C or higher.

[0025]

[Embodiments] A more detailed description of the present invention is provided below with embodiments. A 10 kg ingot of the material for a guide wire was decomposed by vacuum decomposition, and this ingot was cast into a round bar with a diameter of 10 mm. After solution treatment was applied by air cooling at 1,000 to 1,200 °C X 1 hour to the cast round bar, drawing and solution treatment were repeated to gradually make the diameter thinner, and a material in a solution treatment state with a diameter of 0.48 mm prior to the final drawing was prepared. Alloy numbers 1 to 20 in Table 1 are the inventive materials, and alloy numbers 21 to 28 are the comparative materials. The Be content in the present invention is the unadded level. Among the comparative materials, both alloy numbers 26 and 28 are the Elgiloy alloy and Co-Ni-Cr-Fe-based alloy shown in Japanese Patent Document No. H11[1999]-502434 and Unexamined Japanese Patent Application Bulletin No. H06[1994]-63151.

[0026]

[Table 1]

(mass %)

Alloy No.	C	Si	Mn	Co	Ni	Cr	Mo	Ti	Al	Nb	O	S	Be	Fe	Remarks
1	0.08	0.31	1.72	41.2	15.5	20.8	7.2	---	---	---	0.0033	0.0084	0.0021	Remnant	Present invention
2	0.16	0.33	1.65	40.7	16.1	20.2	7.0	---	---	---	0.0041	0.0054	0.0048	Remnant	Present invention
3	0.09	0.41	1.58	32.1	15.7	20.8	6.9	---	---	---	0.0040	0.0082	0.0052	Remnant	Present invention
4	0.06	0.35	1.55	48.3	16.1	20.1	7.3	---	---	---	0.0029	0.0066	0.0064	Remnant	Present invention
5	0.06	0.31	1.81	69.1	10.1	11.5	5.4	---	---	---	0.0021	0.0034	0.0074	Remnant	Present invention
6	0.09	0.44	1.32	40.6	11.3	20.1	6.8	---	---	---	0.0040	0.0087	0.0058	Remnant	Present invention
7	0.10	0.29	1.54	41.3	22.6	20.0	7.6	---	---	---	0.0030	0.0053	0.0046	Remnant	Present invention
8	0.05	0.32	1.43	40.1	32.3	18.9	5.8	---	---	---	0.0044	0.0069	0.0051	Remnant	Present invention
9	0.06	0.26	1.78	40.6	15.6	10.6	7.3	---	---	---	0.0022	0.0022	0.0074	Remnant	Present invention
10	0.08	0.36	1.69	40.9	16.1	15.2	7.5	---	---	---	0.0031	0.0088	0.0063	Remnant	Present invention
11	0.09	0.42	1.53	41.0	16.0	29.1	6.9	---	---	---	0.0036	0.0055	0.0058	Remnant	Present invention
12	0.06	0.25	1.38	40.6	15.8	20.6	4.2	---	---	---	0.0029	0.0069	0.0062	Remnant	Present invention
13	0.07	0.33	1.77	41.4	15.4	20.9	11.5	---	---	---	0.0041	0.00	0.00	Remnant	Present invention
14	0.06	0.38	1.62	41.5	15.8	20.4	18.7	---	---	---	0.0023	0.0077	0.0047	Remnant	Present invention
15	0.10	1.22	1.80	40.6	16.0	20.6	7.2	---	---	---	0.0003	0.0043	0.0086	Remnant	Present invention
16	0.08	0.13	1.62	40.5	15.7	20.1	7.4	---	---	---	0.0082	0.0086	0.0033	Remnant	Present invention
17	0.05	0.27	1.53	41.2	15.5	20.7	7.4	2.0	---	---	0.0031	0.0064	0.0046	Remnant	Present invention
18	0.07	0.38	1.71	40.5	17.1	21.8	7.4	3.1	---	---	0.0038	0.0048	0.0042	Remnant	Present invention
19	0.09	0.57	1.41	42.0	16.8	20.5	7.4	1.7	---	0.5	0.0051	0.0062	0.0035	Remnant	Present invention
20	0.08	0.38	1.65	40.9	16.3	21.3	7.4	1.5	0.2	0.6	0.0044	0.0057	0.0066	Remnant	Present invention
21	0.06	0.65	1.52	29.2	16.7	21.0	7.8	---	---	---	0.0025	0.0069	0.0057	Remnant	Comparative example
22	0.05	0.34	1.73	41.2	9.2	20.5	7.6	---	---	---	0.0045	0.0047	0.0036	Remnant	Comparative example
23	0.06	0.29	1.53	31.3	42.4	17.6	6.0	---	---	---	0.0039	0.0063	0.0057	Remnant	Comparative example
24	0.07	0.42	1.60	41.2	14.8	20.2	2.9	---	---	---	0.0028	0.0051	0.0098	Remnant	Comparative example
25	0.05	0.33	0.33	39.8	16.7	19.3	21.0	---	---	---	0.0031	0.0079	0.0026	Remnant	Comparative example
26	0.04	0.06	1.77	41.2	15.9	20.8	7.5	---	---	---	0.0251	0.0041	0.0344	Remnant	Comparative example
27	0.08	2.30	1.63	40.8	16.7	21.0	7.3	---	---	---	0.0003	0.0031	0.0051	Remnant	Comparative example
28	0.09	0.50	1.53	40.9	16.1	21.0	7.1	---	---	---	0.0151	0.0262	0.0410	Remnant	Comparative example

Note) Among the added elements from C to Nb in Table 1, those items that are not added are indicated with by ---. Among the impurity elements from O to Be, when an items has a numerical value indicated this stands for the amount that mixed in.

[0027] In the production of this material, ...

... an evaluation of the hot working properties was done based on whether or not there are any cracks in the cast bar material, and moreover an evaluation of the cold working properties was done based on whether or not any breakage occurs during drawing. Table 2 shows the results thereof.

[0028]

[Table 2]

Alloy No.	Hot working properties (presence or absence of cracks)	Cold working properties (presence or absence of breakage during drawing)
1	Good	Good
2	Good	Good
3	Good	Good
4	Good	Good
5	Good	Good
6	Good	Good
7	Good	Good
8	Good	Good
9	Good	Good
10	Good	Good
11	Good	Good
12	Good	Good
13	Good	Good
14	Good	Good
15	Good	Good
16	Good	Good
17	Good	Good
18	Good	Good
19	Good	Good
20	Good	Good
21	Good	Good
22	Good	Breakage (drawing not possible)
23	Good	Good
24	Good	Good
25	Good	Breakage (drawing not possible)
26	Good	Breakage (drawing not possible)
27	Good	Breakage (drawing not possible)
28	Cracks (hot working not possible)	---

[0029] The inventive alloys numbers 1 to 20 exhibited good hot working properties and cold working properties. The amount of Ni in comparative alloy number 22 was less than 10%, so it was not softened adequately by solution treatment and therefore breakage occurred during drawing. Since the amount of Mo in comparative alloy number 25 was greater than 20%, the work properties declined, and the cold working properties in particular were poor, so breakage occurred during drawing. In the case of alloy number 26, which was shown in Japanese Patent Document No. H11[1999]-502434 and Unexamined Japanese Patent Application Bulletin No. H06[1994]-63151, the amount of Si was lower than 0.1%, and O was contained in excess of 0.01%, so a large amount of oxides were formed, and breakage occurred during drawing. Since the amount of Si in comparative alloy number 27 was greater than 2%, the cold working properties were poor, so breakage occurred during drawing. In the case of alloy number 28, which was shown in Japanese Patent Document No. H11[1999]-502434 and Unexamined Japanese Patent Application Bulletin No. H06[1994]-63151, the amount of S was greater than 0.02%, so the hot working properties were poor, and cracking occurred during hot working.

[0030] With respect to the materials shown in Table 1, after the final drawing of 60% respectively for each, a sample with a diameter of 0.3 mm was prepared by applying aging, and this was supplied for the respective tests for each one. A tensile test was conducted as the evaluation of the strength, and the tensile strength was calculated. In addition, ...

... a bend test was similarly conducted with a sample with a diameter of 0.3 mm, and Young's modulus was measured. If the tensile strength is 1,800 MPa or above, the strength is good, and if Young's modulus is 180 GPa and above, the hardness is good.

[0031] Using samples that were prepared similarly, a test of the kink resistance was conducted. As shown in the left side figure in Figure 1, when a sample (1) with a diameter (d) of 0.3 mm was wound once on a round bar (2) with a diameter (D) of 15 mm at 37 °C, and it was then released as shown in the right side of the same figure, if the angle created by the lines of both sides of the wound site (the residual angle) is 150° or more, the kink resistance is good. Here the ratio of the round bar diameter to the diameter of material for a guide wire (sample) is set at 50: 1.

[0032] Using samples that were prepared similarly, a test of the torque transferability was conducted. In a state in which a sample with a diameter of 0.3 mm and a length of 1 m was suspended (37 °C), when one end (the handheld part) was rotated, the time required until the other end, to which torque of 11.3 mN•m per unit section area (1 mm^2) (torque of approximately 0.8 mN•M in the present sample with a diameter of 0.3 mm), responded was measured, and the period was also measured in the event that the rotation that occurred due to this response oscillated periodically. If it rotates with this response time being a lag of 25 seconds or less, and moreover either the rotation that occurs due to this response does not oscillate periodically or the period thereof is 20 seconds or less, the torque transferability is good. Table 3 shows these results by summarizing them for inventive alloy numbers 1 and 17 and comparative alloy numbers 21, 23, 24 and 26.

[0033]

[Table 3]

	Production conditions		Strength	Hardness	Kink resistance	Torque transferability		
Alloy No.	Drawing surface reduction rate (%)	Aging temperature (°C)	Tensile strength (MPa)	Young's modulus (GPa)	Residual angle (°)	Response time (s)	Oscillation period (s)	
1	60	500	2355	226	165	14	No oscillation	Present invention
17	60	500	2510	240	166	11	No oscillation	Present invention
21	60	500	1468	165	154	35	25	Comparative example
23	60	500	1432	167	153	37	28	Comparative example
24	60	500	1578	171	155	40	26	Comparative example
26	60	500	2348	224	165	15	No oscillation	Comparative example

[0034] In alloy numbers 1 and 17, which were produced by the inventive production method with the inventive alloys, the strength, hardness, kink resistance and torque transferability are good. In the case of alloy number 26, which was shown in Japanese Patent Document No. H11[1999]-502434 and Unexamined Japanese Patent Application Bulletin No. H06[1994]-63151, breakage occurred during drawing, but the test was conducted by selectively sampling the portion where the occurrence of breakage was minor. The results were that the strength, hardness, kink resistance and torque transferability were equivalent to or better than those of alloy number 26. In the case of number 17 in particular, by adding Ti, the strength, hardness and torque transferability were improved. In this manner, while inventive alloy numbers 1 and 17 maintained superior strength, hardness, kink resistance and torque transferability, the harmfulness, embrittlement and hot working properties during production were improved. In the cases of comparative alloy numbers 21, 23 and 24 respectively, the amount of Co added was insufficient, the amount of Ni added was excessive and the amount of Mo added was insufficient, so the strength, hardness and torque transferability declined markedly.

[0035]

[Effects of the Invention] According to the present invention, it is possible to improve vastly the harmfulness, embrittlement and hot working properties in the process of production of the material for a guide wire are solved while still providing strength, hardness, kink resistance and torque transferability as well, and this is a technique that is indispensable for practical application of guide wires.

[Brief Description of the Figures]

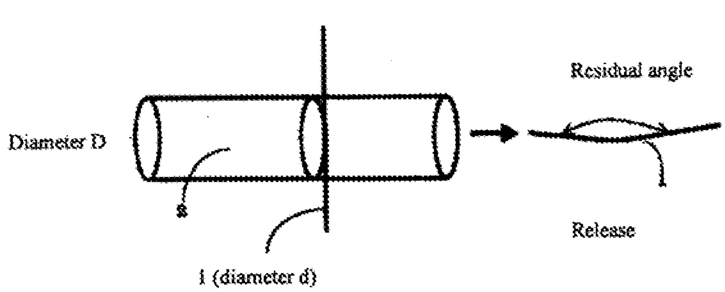
[Figure 1] This is an explanatory figure showing the kink resistance test method.

[Figure 2] This is an explanatory figure showing the torque transferability test data.

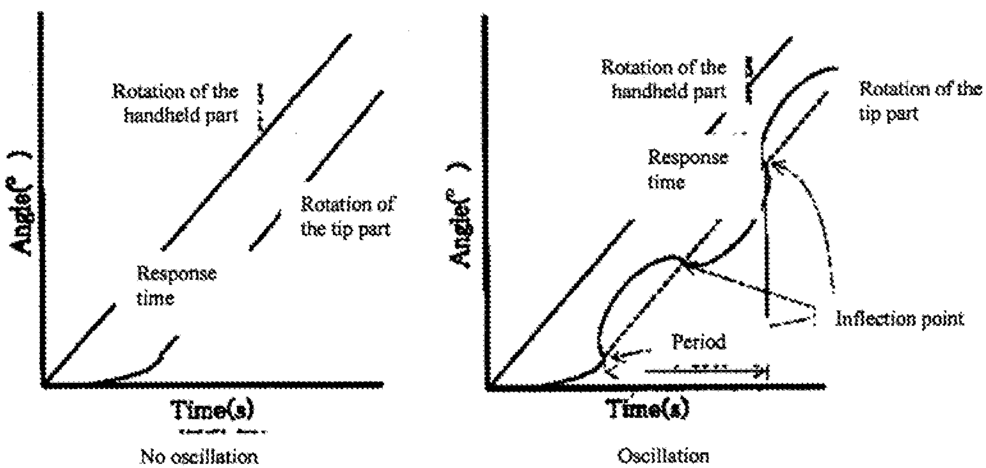
[Explanation of the Key]

1. Material for a guide wire
2. Round bar

[Figure 1]



[Figure 2]



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(72) Inventor: Toshihiro UEHARA
Hitachi Research Laboratory, Hitachi Metals KK
2107-2 Yasugi-cho, Yasugi-shi, Shimane-ken

(72) Inventor: Shun'ichi UCHINO
Terumo KK
150 Maimaigi-cho, Fujinomiya -shi, Shizuoka-ken

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CERTIFICATE OF TRANSLATION

February 9, 2011

I, John K. Marchioro, hereby certify that I am competent in both Japanese and English languages.

I further certify under penalty of perjury that translation of the aforementioned patent document:

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(71)出願人　000005083
日立金属株式会社
東京都港区芝浦一丁目２番１号

(71)出願人　000109543
テルモ株式会社
東京都渋谷区幡ヶ谷２丁目44番１号

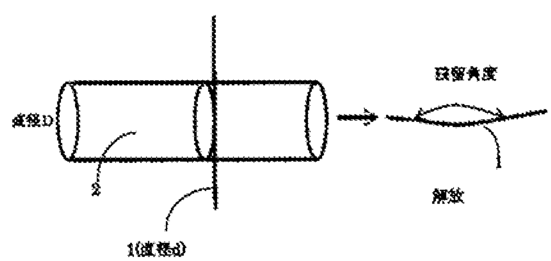
(72)発明者　山口　基
島根県安来市安来町2107番地２　日立金属株式会社冶金研究所内

(74)代理人　100074848
弁理士　森田　寛

最終頁に続く

(54)【発明の名称】　ガイドワイヤ用材料及びその製造方法

(57)【要約】
【課題】　ガイドワイヤ用材料の製造中における有害性、脆化及び熱間加工性の問題を解決し、さらに強度、剛性、耐キンク性及びトルク伝達性を具備したガイドワイヤ用材料及びその製造方法を提供する。
【解決手段】　質量%でC0.2%以下、Si0.1～2.0%、Mn0.1～3.0%以下、Co30～76%、Ni10～40%、Cr10～30%、Mo3～20%、不純物であるOは0.01%以下、S0.02%以下、Be0.03%未満(0%を含む)、残部は実質的にFeからなるガイドワイヤ用材料である。



【特許請求の範囲】

【請求項１】　質量%でC:0.2 %以下、Si:0.1〜2.0 %、Mn:0.1〜3.0 %以下、Co:30 〜76%、Ni:10 〜40 %、Cr:10 〜30%、Mo:3〜20%、不純物であるOは0.01 %以下、S:0.02%以下、Be:0.03 %未満(0% を含む)、残部は実質的にFeからなることを特徴とするガイドワイヤ用材料。

【請求項２】　更に質量%でTi、Al、Nbのうち一種または二種以上の合計で5 %未満含有することを特徴とする請求項１に記載のガイドワイヤ用材料。

【請求項３】　直径（D）が、ガイドワイヤ用材料の直径（d）対比でD：d＝25〜80：1 となっている丸棒の外周に沿ってガイドワイヤ用材料を一回巻き付けて解放した際、巻き付けた部位の両側の線がなす角度が150 °以上であることを特徴とする請求項１または２に記載のガイドワイヤ用材料。

【請求項４】　長さ1mのガイドワイヤ用材料の一端を中心軸の周りに回転させた時に前記材料の単位断面積(1mm^2)当たり11.3mN m のトルクを負荷されている他端が25秒以内の遅れで応答して回転し、かつ前記応答して起こる回転は周期的に振動しないか若しくはその周期が20秒以内であることを特徴とする請求項１乃至３の何れかに記載のガイドワイヤ用材料。

【請求項５】　請求項１乃至４の何れかに記載のガイドワイヤ用材料の製造方法であって、減面率20% 以上の冷間加工後に300 〜700 ℃の時効処理を行うことを特徴とするガイドワイヤ用材料の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、医療用器具であるカテーテルを血管、心臓、消化管、気管、その他体腔内の所定部位まで導入するためのガイドワイヤ用材料とその製造方法に関するものである。

【０００２】

【従来の技術】カテーテルを血管などの所定部位に導入する場合、案内用にガイドワイヤを目的部まで導入する。複雑に分岐し曲がりくねった血管等に対応できるように、ガイドワイヤの先端部分に十分な柔軟性がなければならない。ガイドワイヤの先端部を細くすることや異種材料を先端部のみに接合させることによりこの柔軟性を確保している。また、血管等の体腔内部にてガイドワイヤをコントロールするために手元操作部において外科医が操作した回転が実質的に全て先端部に伝達し（トルク伝達性）、かつ血管等の中で座屈することがなく押出せるように十分な強度 剛性が必要となる。

【０００３】強度 剛性は特にガイドワイヤを操作する医師の手元側で特に必要とされ、更に曲がりくねった血管等の中を通ってもガイドワイヤがキンク現象（永久変形）を発生しないことが必要である。このキンク現象が発生すると回転が好ましい状態で伝達されず、手元で操作した回転がむち打ち状の運動となって伝わってしまう。以上のようにガイドワイヤ用材料として必要な特性は強度 剛性、トルク伝達性、耐キンク性及び必要に応じて柔軟性が求められ、特に強度 剛性、トルク伝達性、耐キンク性については材料に必須で求められる特性である。

【０００４】従来、このような特性が求められるガイドワイヤ用材料には、冷間塑性加工を加えて強度を大幅に高めたSUS304またはSUS302タイプ(JIS G4309) のステンレス鋼（例えば特開平11-299899 号、特開平06-063150 号など）及び超弾性合金であるNi-Ti 合金（例えば特開2001-009041 号、特開平11-128363)が多く用いられている。しかしながら、ステンレス鋼は強度 剛性及びトルク伝達性の点に付いては従来の材料の中では有利なものの改善の余地があり、耐キンク性については不十分である。Ni-Ti 合金は耐キンク性には優れているものの、強度 剛性、トルク伝達性は著しく劣っていた。

【０００５】

【発明が解決しようとする課題】上述の問題に対して、優れたトルク伝達性を有しながら、耐キンク性や強度 剛性を改善したCo-Ni-Cr-Fe 系合金及びElgiloy(エルジロイカンパニー社の商標：以下、単にElgiloy 合金と記す）合金をガイドワイヤに用いる提案がなされている。具体的には、耐キンク性を改善した例として特表平11-502434 号にはガイドワイヤのシャフト材料としてElgiloy 合金を用いることが提案され、また、強度 剛性を改善した例として特開平6-63151 号にはガイドワイヤ用材料としてElgiloy 合金と同様な組成のCo-Ni-Cr-Fe 合金を用いることが開示されている。

【０００６】上述した特表平11-502434 号及び特開平6-63151 号に開示されているElgiloy合金及びCo-Ni-Cr-Fe 合金は、強度 剛性、トルク伝達性及び耐キンク性の点では有利であるものの、これらElgiloy 合金及びCo-Ni-Cr-Fe 合金は有害な元素であるBeを少量含有しているため、ガイドワイヤ用材料製造時に人体に悪影響がある可能性が心配される。Beの問題は、Elgiloy 合金やそれに類似したCo-Ni-Cr-Fe 合金からなるガイドワイヤを実用化する上で問題となる可能性がある。

【０００７】また、これらの合金はSiを無添加としているため、脱酸が十分でなく、O が多量に残存してガイドワイヤ用材料が脆化し、冷間加工時や使用時に破断することが心配される。更に、特表平11-502434 号及び特開平6-63151 号に開示されるElgiloy 合金やCo-Ni-Cr-Fe 合金では、不純物元素のS 量が考慮されておらず、S含有により熱間加工性が悪く、製造に必須の工程である熱間加工時に割れを発生するという問題があった。本発明の目的は、従来から用いられてきたElgiloy 合金やCo-Ni-Cr-Fe 合金が有する優れた強度 剛性、トルク伝達性、耐キンク性を維持しながら、ガイドワイヤ用材料の製造中における有害性、脆化及び熱間加工性の問題を解

決したガイドワイヤ用材料及びその製造方法を提供することである。

【0008】

【課題を解決するための手段】本発明者等は、ガイドワイヤ用材料の製造中における有害性、脆化及び熱間加工性の問題を検討した結果、Siを必要最低限添加し、不純物であるO 量及びS 量を低く抑え、更にBeを無添加(0%)として、不純物レベルに迄制御することでその製造時における有害性、脆化及び熱間加工性を改善できることを見いだし本発明に到達した。

【0009】即ち本発明は、質量%でC:0.2 %以下、Si:0.1～2.0 %、Mn:0.1～3.0 %以下、Co:30 ～76%、Ni:10 ～40%、Cr:10 ～30%、Mo:3～20%、不純物であるO は0.01%以下、S:0.02%以下、Be:0.03 %未満(0%を含む)、残部は実質的にFeからなるガイドワイヤ用材料である。好ましくは、質量%でTi、Al、Nbのうち一種または二種以上の合計で5 %未満含有するガイドワイヤ用材料である。

【0010】また本発明は、直径（D）が、ガイドワイヤ用材料の直径（d）対比でD：d＝25～80：1 となっている丸棒の外周に沿ってガイドワイヤ用材料を一回巻き付けて解放した際、巻き付けた部位の両側の線がなす角度が150 °以上であるガイドワイヤ用材料であり、長さ1mのガイドワイヤ用材料の一端を37℃において中心軸の周りに回転させた時に単位断面積($1mm^2$ ）当たり11.3 mN・m のトルクを負荷されている他端が25秒以内の遅れで応答して回転し、かつ前記応答して起こる回転は周期的に振動しないか若しくはその周期が20秒以内であるガイドワイヤ用材料である。

【0011】また本発明は、上述のガイドワイヤ用材料の製造方法として、減面率20% 以上の冷間加工後に300 ～700 ℃の時効処理を行うガイドワイヤ用材料の製造方法である。

【0012】

【発明の実施の形態】上述したように、本発明の重要な特徴はガイドワイヤ用材料として、従来から用いられてきたElgiloy 合金やCo-Ni-Cr-Fe 合金が有する優れた強度・剛性、トルク伝達性、耐キンク性を維持しながら、Siを必要最低限添加し、不純物であるO 量及びS 量を低く抑え、更にBeを無添加(0%)として不純物レベルに迄制御することでガイドワイヤ用材料の製造中における有害性、脆化及び熱間加工性を改善したことにある。以下に各元素の作用について説明する。

【0013】C は基地中に固溶し基地を固溶強化するだけでなく、Cr等と結びついて炭化物を形成し、弾性限を高め、結晶粒粗大化を防止する効果がある。しかし、過度の添加は基地の加工硬化を大きくし、また多量の炭化物形成により冷間加工性を低下させ、また基地中のCrの欠乏を招き耐食性を低下させる。従って、C は0.2 %以下に限定する。好ましくは0.15% 以下である。Siは溶湯に対して強力な脱酸作用を発揮するほか、鋳造性を向上させる作用があるため、本発明においてはSiの添加は必須である。但し、Siが0.1 %より少ないとO 含有量が多くなり、O が大量に残存してガイドワイヤ用材料を脆化させる。一方、2.0 %を超えて添加すると冷間加工性が低下するためSiは0.1 ～2.0 %とし、好ましいSiの含有量は0.1 ～1.0%の範囲である。

【0014】MnはSiと同じく脱酸作用を発揮する他、鋳造性を向上させる作用があるが、過度の添加はεCo相の析出を阻害して、強度・剛性の低下を招くためMnは0.1 ～3.0 %と規定した。好ましくは1.0 ～2.5%の範囲である。Coは本合金の基地となる元素であり、冷間加工と時効処理によりαCo相からεCo相に変態し、更に時効処理により金属間化合物を析出して強度・剛性及びトルク伝達性を向上させる。Coは30%より少ないと効果がなく、一方、76%を超えて添加してもより一層の強度向上効果がないことからCoは30～76%と規定した。好ましくは35～45% の範囲である。

【0015】Niは固溶化処理により冷間加工可能な硬さに軟化させ、時効処理においてはTi及び/ またはAlと結びついてγ' 相を析出し、硬化に寄与する元素である。Niは10%より少ないと効果が少なく、一方、40%を超えて添加すると強度・剛性及びトルク伝達性向上に必要なεCo相への変態を阻害するため、Niの添加量は10～40%と規定した。好ましくは10～20% の範囲である。Crは炭化物を形成して弾性限向上させ、また、基地中に固溶して、体内に挿入されたときに必要となる耐食性を維持する元素であり、そのためには10%以上の添加が必要である。しかし、30%を超えて添加すると冷間加工性が低下するためCrは10～30%とする。好ましくは15～25% の範囲である。

【0016】Moは基地に固溶し、強度及び耐食性を向上させるだけでなく、更に一部は時効処理によって金属間化合物を析出して強度、剛性及びトルク伝達性を向上させる元素である。Moは3 %より少ないと十分な効果が得られず、一方、20%を超えて添加すると加工性を低下させるためMoの添加量は3 ～20%とする。好ましくは5～15% の範囲である。FeはNi同様冷間加工性を向上させる元素であり、本発明で規定する各元素の残部となる。しかしながら、過度に含有するとεCo相への変態を阻害するなど、強度・剛性及びトルク伝達性を低下させるため、Feの好ましい上限は46%であり、より好ましくは20%以下である。

【0017】次に本発明で制限すべき不純物元素について説明する。先ず、O は溶製時に材料内に不可避に混入する不純物元素であり、材料を脆化させる元素である。そのため脱酸効果を有するSi及びMnの複合添加により極力低減する必要がある。O が0.01%より多いと酸化物系の介在物が多く形成され、冷間加工時や使用時に破断する可能性があることからO は0.01%以下とする。好まし

くは0.005%以下の範囲である。S は溶製時に材料内に不可避に混入する不純物元素であり、熱間加工性を低下させる元素であるためS 含有量が少ない原料の選択、真空溶解、スラグ脱硫等により極力低減する必要がある。S は0.02%より多いと熱間加工性が大幅に低下することからS は0.02% 以下とする。好ましくは0.01% 以下である。

【0018】Beは時効析出により強靭性を増す元素であるが、ガイドワイヤ用材料製造時に有害となる可能性があるため無添加(0%)レベルに制御する必要がある。例えばBeを無添加(0%)としても本発明合金では剛性、強度、耐キンク性、トルク伝達性及びその他のガイドワイヤに必要とされる特性に影響はない。Beの製造中における有害性をなくすためには最大限含有しても0.03%未満に抑える必要がある。さらに好ましくは0.01%以下がよい。

【0019】次に本発明で規定する選択元素について説明する。Ti、Al及びNbは時効処理時にNiと結びついてNi3(Ti、Al、Nb) のγ' またはγ''相を析出させ、強度、剛性及びトルク伝達性を向上させる元素であるため、必要に応じて添加する。しかし、過度の添加は加工性を低下させるためTi、Al、Nbの添加量は一種または二種以上の合計で5 %未満とする。なお、本発明ではこれら説明してきた元素以外の不可避的に含有される不純物元素は、特に規定するものではないが、以下の元素は質量%にて下記の範囲で本発明の材料に含まれてもよい。

P ≦0.04%、Cu≦0.30%、V ≦0.5 %、Ta≦0.5 %、Ca≦0.02%、Mg≦0.1 %、N ≦0.1 %、B ≦0.01%

【0020】次に、上述した本発明のガイドワイヤ用材料は、最適な製造方法と組み合わせることで、以下の特性を満足することができる。曲がりくねった血管内を通る際にキンク現象を起こさないためには図1に示すように直径（D ）の丸棒(2) と直径（d ）のガイドワイヤ用材料(1) をD：d＝25～80：1 の比率になるように用意し、37℃において丸棒(2) にガイドワイヤ用材料(1) を一回巻き付けて解放した際、巻き付けた部位の両側の線がなす角度が150 °以上であることが重要であり、優れた耐キンク性が得られているかを知るための重要な指標となる。ここで、丸棒直径（D）とガイドワイヤ用材料直径（d）の比率を25～80：1にするのは、体内で湾曲する血管を想定して、最も過酷な条件を付与するためである。そして、ガイドワイヤ用材料を一回巻き付けて解放した際、巻き付けた部位の両側の線がなす角度が150 °以上であれば、耐キンク性が優れているものと判断できる。

【0021】また次に、本発明のガイドワイヤ用材料をガイドワイヤとして用いた時、血液等の抵抗により、トルクが負荷された状態となる。実際には、血液（血流）の抵抗がある中で、医師によってガイドワイヤ手元部で加えられた回転が数十cm～約1m先の先端部が回転するまでの時間が短時間であること、更に回転によってガイドワイヤ自体が周期的に振動しないか、または周期的に振動しても周期が20秒以内でなければ、ガイドワイヤ自体の操作性が著しく低下する。そのため、血液（血流）の抵抗を想定して、37℃において他端にガイドワイヤ用材料の単位断面積(1mm²）当たり11.3mN m のトルクが負荷された状態で、1mの長さのガイドワイヤ用材料において手元部となる一端での中心軸の周りでの回転が応答時間25秒以内の遅れで他端に伝達することがガイドワイヤ用材料に求められる。ここで規定する長さ1mのガイドワイヤ用材料の一端を中心軸の周りに回転させた時に前記ガイドワイヤ用材料の単位断面積(1mm²）当たり11.3mN m のトルクを負荷されている他端が25秒以内の遅れで応答して回転し、かつ前記応答して起こる回転は周期的に振動しないか若しくはその周期が20秒以内であることを満足していれば良好なトルク伝達性が得られていると判断できる。

【0022】なお、ここで言う応答時間とは図2の左図に示すように回転を開始してある程度の時間が経過した後、手元部の回転が先端部（他端）に伝わるまでの時間を言い、特に先端部の回転に振動がある場合は先端部の回転を示す曲線の変曲点における応答時間を採ると良い。先端部の回転に振動がある場合の周期は、例えば図2の右図に示すように変曲点3 点分の時間を採るなどの方法で、基本的に同位相から同位相までの時間を採れば良い。

【0023】次に、本発明の製造方法について説明する。冷間加工及び時効処理は本発明のガイドワイヤ用材料をガイドワイヤとして用いるために必須の工程であり、本発明で規定する化学組成を満たした上で、冷間加工及び時効処理を施さなければ、強度 剛性、トルク伝達性、耐キンク性を同時に満足することはできない。冷間加工及び時効処理を施すことによりαCo相の一部がεCo相へ変態し、更に時効処理時に金属間化合物及び炭化物が析出することで強度、剛性及びトルク伝達性が著しく向上する。冷間加工時の減面率が20%未満の場合及び時効処理温度300 ℃未満または700 ℃を超えるとεCo相への変態が十分でなく、また、この時効処理温度では析出による強度、剛性及びトルク伝達性の向上を充分に得ることができない。特に700 ℃を超える温度ではεCoが分解してしまう。従って、冷間加工の減面率は20%以上とし、それに続く時効処理温度は300 ～700 ℃とする。好ましい冷間加工の減面率は40%以上であり、時効処理温度は450 ～600 ℃である。

【0024】また、本発明の温度範囲で時効処理を施すことにより耐キンク性が向上する。時効処理により冷間加工で与えられた歪みが回復し、低減される。例えば引抜きのような冷間加工では引張方向に歪みが与えられ、その後の時効処理によりその歪みが低減される。引張方向の歪みが残存すると、ガイドワイヤ用材料を曲げた時に材料の内側には圧縮応力がかかるのでバウシンガー効

果により低い歪み量で降伏する現象が発生する。そのため大きな曲率で曲げても塑性変形しやすくなり、耐キンク性が低下する。従って、時効処理は耐キンク性向上のために必須の工程であり、さらに時効温度が低すぎても回復せずに引張り歪みが残存するので、この意味からも時効処理温度は300 ℃以上であることが必要である。

【0025】

【実施例】以下に実施例として本発明を詳しく説明する。真空溶解によりガイドワイヤ用材料の10kgインゴットを溶解し、このインゴットを直径10mmの棒材に鍛造した。鍛造した棒材に1000～1200℃×1h空冷による溶体化処理を施した後、引抜きと溶体化処理を繰返して直径を細くしていき、最終引抜き前の直径0.48mmの溶体化処理状態の素材を準備した。ガイドワイヤ用材料の組成を表に示す。表1の合金No. 1～20は本発明材であり、合金No.21 ～28は比較材である。本発明のBe含有量は無添加レベルである。なお、比較材のうち、合金No.26 及び28はともに特表平11-502434 号及び特開平6-63151 号に示されているElgiloy 合金及びCo-Ni-Cr-Fe 合金である。

【0026】

【表1】

(mass%)

合金No.	C	Si	Mn	Co	Ni	Cr	Mo	Ti	Al	Nb	O	S	Be	Fe	備考
1	0.08	0.31	1.72	41.2	15.5	20.8	7.2	—	—	—	0.0033	0.0084	0.0021	残部	本発明
2	0.16	0.33	1.65	40.7	16.1	20.2	7.0	—	—	—	0.0041	0.0054	0.0048	残部	本発明
3	0.09	0.41	1.58	32.1	15.7	20.8	6.9	—	—	—	0.0040	0.0082	0.0052	残部	本発明
4	0.06	0.35	1.55	48.3	16.1	20.1	7.3	—	—	—	0.0029	0.0066	0.0064	残部	本発明
5	0.06	0.31	1.81	69.1	10.1	11.5	5.4	—	—	—	0.0021	0.0034	0.0074	残部	本発明
6	0.09	0.44	1.32	40.6	11.3	20.1	6.8	—	—	—	0.0040	0.0087	0.0058	残部	本発明
7	0.10	0.29	1.54	41.3	22.6	20.0	7.6	—	—	—	0.0030	0.0053	0.0046	残部	本発明
8	0.05	0.32	1.43	40.1	32.3	18.9	5.8	—	—	—	0.0044	0.0069	0.0051	残部	本発明
9	0.06	0.26	1.78	40.6	15.6	10.6	7.3	—	—	—	0.0022	0.0022	0.0074	残部	本発明
10	0.08	0.36	1.69	40.9	16.1	15.3	7.5	—	—	—	0.0031	0.0088	0.0063	残部	本発明
11	0.09	0.42	1.53	41.0	16.0	29.1	6.9	—	—	—	0.0036	0.0055	0.0058	残部	本発明
12	0.06	0.25	1.38	40.6	15.8	20.6	4.2	—	—	—	0.0029	0.0069	0.0062	残部	本発明
13	0.07	0.33	1.77	41.4	15.4	20.9	11.5	—	—	—	0.0041	0.0077	0.0047	残部	本発明
14	0.06	0.38	1.62	41.5	15.8	20.4	18.7	—	—	—	0.0023	0.0043	0.0086	残部	本発明
15	0.10	1.22	1.80	40.6	16.0	20.6	7.2	—	—	—	0.0003	0.0086	0.0033	残部	本発明
16	0.08	0.13	1.62	40.5	15.7	20.1	7.4	—	—	—	0.0082	0.0064	0.0046	残部	本発明
17	0.05	0.27	1.53	41.2	15.5	20.7	7.4	2.0	—	—	0.0031	0.0048	0.0042	残部	本発明
18	0.07	0.38	1.71	40.5	17.1	21.8	7.4	3.1	—	—	0.0038	0.0062	0.0035	残部	本発明
19	0.09	0.57	1.41	42.0	16.8	20.5	7.4	1.7	—	0.5	0.0051	0.0071	0.0051	残部	本発明
20	0.08	0.38	1.65	40.9	16.3	21.3	7.4	1.5	0.2	0.6	0.0044	0.0057	0.0066	残部	本発明
21	0.06	0.65	1.52	29.2	16.7	21.0	7.8	—	—	—	0.0025	0.0069	0.0057	残部	比較例
22	0.05	0.34	1.73	41.2	9.2	28.5	7.6	—	—	—	0.0045	0.0047	0.0036	残部	比較例
23	0.06	0.29	1.53	31.3	42.4	17.6	6.0	—	—	—	0.0039	0.0063	0.0057	残部	比較例
24	0.07	0.42	1.60	41.2	14.8	20.2	2.9	—	—	—	0.0028	0.0051	0.0098	残部	比較例
25	0.05	0.33	1.59	39.8	16.7	19.3	21.0	—	—	—	0.0031	0.0079	0.0026	残部	比較例
26	0.04	0.06	1.77	41.2	15.9	20.8	7.5	—	—	—	0.0251	0.0041	0.0344	残部	比較例
27	0.08	2.30	1.63	40.8	16.7	21.0	7.3	—	—	—	0.0003	0.0031	0.0051	残部	比較例
28	0.09	0.50	1.53	40.9	16.1	21.0	7.1	—	—	—	0.0151	0.0262	0.0410	残部	比較例

注）表1でCからNbまでの添加元素のうち無添加のものは－で示し、OからBeまでの不純物元素のうち数値で示してあるものは、混入量を示す。

【0027】この素材作製において、鍛造した棒材にお

ける割れの有無により熱間加工性を評価し、さらに引抜き時の破断発生有無により冷間加工性を評価した。その結果を表2に示す。

【0028】

【表2】

合金No.	熱間加工性(割れの有無)	冷間加工性(引抜き時破断有無)
1	良好	良好
2	良好	良好
3	良好	良好
4	良好	良好
5	良好	良好
6	良好	良好
7	良好	良好
8	良好	良好
9	良好	良好
10	良好	良好
11	良好	良好
12	良好	良好
13	良好	良好
14	良好	良好
15	良好	良好
16	良好	良好
17	良好	良好
18	良好	良好
19	良好	良好
20	良好	良好
21	良好	良好
22	良好	破断(引抜き不可)
23	良好	良好
24	良好	良好
25	一部割れ	破断(引抜き不可)
26	良好	破断(引抜き不可)
27	良好	破断(引抜き不可)
28	割れ(熱間加工不可)	—

【0029】本発明合金No. 1～20は良好な熱間加工性及び冷間加工性を示した。比較合金No. 22 はNiが10%より低いため溶体化処理により充分軟化しなかったため引抜き中に破断が発生した。比較合金No. 25 はMoが20%より多いため加工性が低下し、特に冷間加工性が悪いため引抜き中に破断が発生した。特表平11−502434 号及び特開平6−63151 号に示されている合金No. 26 はSiが0.1 %より低く、O が0.01%を超えて含まれているため多量の酸化物が形成され、引抜き中に破断が発生した。比較合金No. 27 はSiが2 %より多いため冷間加工性が悪く、引抜き中に破断が発生した。特表平11−502434 号及び特開平6−63151 号に示されている合金No. 28はS が0.02%より多いため熱間加工性が悪く、熱間加工中に割れが発生した。

【0030】表1に示す材料についてそれぞれ60%の最終引抜き後、時効処理を施すことにより、直径0.3mm の試料を準備し、それぞれ試験に供した。強度の評価として引張試験を行い、引張強さを求めた。また同じく直径

0.3㎜の試料を用いて曲げ試験を行い、ヤング率を測定した。引張強さは1800MPa以上であれば強度が良好であり、ヤング率は180GPa以上であれば剛性は良好である。

【0031】同様に準備した試料を用いて、耐キンク性の試験を行った。図1の左側図に示すように37℃にて直径（D）が15㎜の丸棒(2)に直径（d）0.3㎜の試料(1)を一回巻き付けて同図右側に示すように解放した際、巻き付けた部位の両側の線がなす角度（残留角度）が150°以上であれば耐キンク性は良好である。ここでは丸棒直径：ガイドワイヤ材料（試料）直径=50：1とした。

【0032】同様に準備した試料を用いて、トルク伝達性の試験を行った。直径0.3㎜長さ1mの試料を吊るした状態(37℃)で、一端（手元部）を回転させた時に単位断面積(1㎜²)当たり11.3mN m のトルク（直径0.3㎜の本試料において約0.8mN m のトルク）を負荷されている他端（先端部）が応答する時間測定し、さらにこの応答により起こる回転が周期的に振動した場合にはその周期も測定した。この応答時間が25秒以内の遅れで回転し、かつこの応答して起こる回転が周期的に振動しないかもしくはその周期が20秒以内であればトルク伝達性は良好である。これらの結果を本合金No.1、17、比較合金21、23、24及び26についてまとめて表3に示す。

【0033】

【表3】

	製造条件		強度	剛性	耐ｷﾝｸ性	トルク伝達性		
合金No	引抜減面率(%)	時効処理温度(℃)	引張強さ(MPa)	ﾔﾝｸﾞ率(GPa)	残留角度(°)	応答時間(s)	振動周期(s)	
1	60	500	2355	226	165	14	振動なし	本発明
17	60	500	2510	240	166	11	振動なし	本発明
21	60	500	1468	165	154	35	25	比較例
23	60	500	1432	167	153	37	28	比較例
24	60	500	1578	171	155	40	26	比較例
26	60	500	2348	224	165	15	振動なし	比較例

【0034】本発明合金で本発明による製造方法により作製した合金No.1及び17は強度、剛性、耐キンク性及びトルク伝達性が良好である。特表平11-502434号及び特開平6-63151号に示されている合金No.26は引抜き中に破断が発生したが、破断の発生が少なかった部分を選択的に採取して試験を行った。その結果No.1及び17の強度、剛性、耐キンク性及びトルク伝達性は合金No.26と同等またはそれ以上であった。特にNo.17ではTiを添加することにより、強度、剛性及びトルク伝達性がより向上している。このように本発明の合金No.1及び17は優れた強度、剛性、耐キンク性及びトルク伝達性を維持しながら、製造中における有害性、脆化及び熱間加工性が改善されている。比較合金No.21、23及び24はそれぞれCo添加量不足、Ni過剰添加及びMo添加量不足のため強度、剛性及びトルク伝達性が著しく低下している。

【0035】

【発明の効果】本発明によれば強度、剛性、耐キンク性及びトルク伝達性を具備したままガイドワイヤ用材料の製造中における有害性、脆化及び熱間加工性を飛躍的に改善することができ、ガイドワイヤの実用化にとって欠くことのできない技術となる。

【図面の簡単な説明】

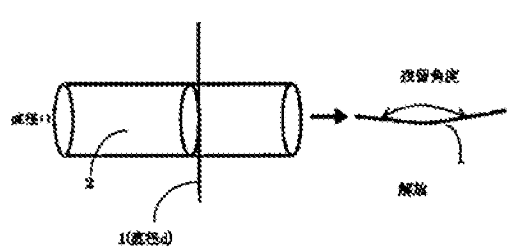
【図1】耐キンク性試験方法を示す説明図である。

【図2】トルク伝達性試験データを示す説明図である。

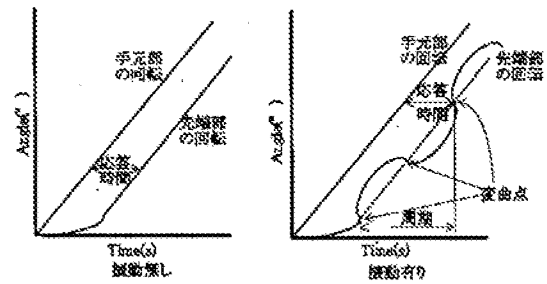
【符号の説明】

1、ガイドワイヤ用材料　2、丸棒

【図1】



【図2】



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(72)発明者　上原　利弘
島根県安来市安来町2107番地２　日立金属株式会社冶金研究所内

(72)発明者　内野　俊一
静岡県富士宮市舞々木町150番地　テルモ株式会社内

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